

1 **PROCESS FOR UPGRADING FISCHER-TROPSCH PRODUCTS**
2 **USING DEWAXING AND HYDROFINISHING**

3
4 FIELD OF THE INVENTION

5
6 The invention relates to a process for upgrading the hydrocarbons having an
7 initial boiling point above about 120 degrees C recovered from a Fischer-
8 Tropsch plant by bulk dewaxing a C₅ plus hydrocarbon Fischer-Tropsch
9 syncrude followed by hydrofinishing and recovering diesel and lubricating
10 base oil products having improved properties.

11
12 BACKGROUND OF THE INVENTION

13
14 The market for lubricating base oils of high paraffinicity is continuing to grow
15 due to the high viscosity index, oxidation stability, and low volatility relative to
16 viscosity of these oils. The products produced from the Fischer-Tropsch
17 process (syncrude) contain a high proportion of wax which make them ideal
18 candidates for processing into lubricating base stocks. Accordingly, the
19 hydrocarbon products recovered from the Fischer-Tropsch process have been
20 proposed as feedstocks for preparing high quality lubricating base oils. See,
21 for example, US Patent 6,080,301 which describes a premium lubricating
22 base oil having a high non-cyclic isoparaffin content prepared from Fischer-
23 Tropsch waxes by hydroisomerization dewaxing and solvent dewaxing.

24
25 High quality diesel products also may be prepared from the syncrude
26 recovered from the Fischer-Tropsch process. Fischer-Tropsch derived diesel
27 typically has a very low sulfur content and an excellent cetane number.
28 These qualities make Fischer-Tropsch derived diesel an excellent blending
29 stock for upgrading lower quality petroleum-derived diesel.

30
31 In general, for the purposes of this disclosure, diesel is considered as having
32 a upper boiling point of about 700 degrees F (370 degrees C) and an initial
33 boiling point of about 300 degrees F (about 150 degrees C). Lubricating base
34 oils typically will have an initial boiling point above about 600 degrees F

1 as, for example, the presence of unsaturated bonds, branching, and
2 heteroatoms in the molecule. Therefore, some hydrocarbons may be present
3 in this fraction which contain less than 5 carbon atoms. Products recovered
4 from the Fischer-Tropsch synthesis which are normally in the gaseous phase
5 at ambient temperature are referred to as C₄ minus product in this disclosure.
6 LPG which is primarily a mixture of propane and butane is an example of a C₄
7 minus product.

8
9 Fractions boiling in the range of diesel may also be referred to as C₁₀ to C₁₉
10 hydrocarbons. Likewise, Fischer-Tropsch wax preferably is comprised
11 predominantly of "C₂₀ plus product" which refers to a product comprising
12 primarily hydrocarbons having more than 20 carbon atoms in the backbone of
13 the molecule and having an initial boiling point at the upper end of the boiling
14 range for diesel. It should be noted that the upper end of the boiling range for
15 diesel and the lower end of the boiling range for Fischer-Tropsch wax have
16 considerable overlap. The term "naphtha" when used in this disclosure refers
17 to a liquid product having between about C₅ to about C₉ carbon atoms in the
18 backbone and will have a boiling range generally below that of diesel but
19 wherein the upper end of the boiling range will overlap that of the initial boiling
20 point of diesel. C₁₀ plus hydrocarbons generally boil above the range of
21 naphtha, i.e., the fractions boiling within the range of diesel and lubricating
22 base oils or above about 150 degrees C. The precise cut-point selected for
23 each of the products in carrying out the distillation operation will be
24 determined by the product specifications and yields desired.

25
26 The dewaxing and hydrofinishing of C₂₀ plus hydrocarbons, including Fischer-
27 Tropsch-derived syncrude is discussed in US Patent 5,135,638. The
28 isomerization of lighter feeds boiling in the range of naphtha and diesel by
29 contacting the feed with a catalyst containing a silicoaluminophosphate
30 molecular sieve (SAPO) is discussed in US Patent 4,859,311.

31
32 As used in this disclosure the words "comprises" or "comprising" is intended
33 as an open-ended transition meaning the inclusion of the named elements,
34 but not necessarily excluding other unnamed elements. The phrase "consists

1 essentially of" or "consisting essentially of" is intended to mean the exclusion
2 of other elements of any essential significance to the composition. The
3 phrases "consisting of" or "consists of" are intended as a transition meaning
4 the exclusion of all but the recited elements with the exception of only minor
5 traces of impurities.

6 7 SUMMARY OF THE INVENTION 8

9 Broadly, the present invention is directed to a process for producing low pour
10 point hydrocarbon products having an initial boiling point above about 150
11 degrees C from a Fischer-Tropsch plant which comprises (a) recovering a
12 feedstock comprising C₅ plus syncrude from a Fischer-Tropsch plant; (b)
13 dewaxing the C₅ plus syncrude feedstock in a catalytic dewaxing zone by
14 contacting the C₅ plus syncrude feedstock with a dewaxing catalyst under
15 dewaxing conditions, whereby a C₅ plus intermediate is produced having a
16 lowered pour point relative to the C₅ plus syncrude feedstock; (c)
17 hydrofinishing the C₅ plus intermediate in a hydrofinishing zone under
18 hydrofinishing conditions, whereby a UV stabilized C₅ plus product is
19 produced; and (d) separately collecting from the UV stabilized C₅ plus product
20 a low pour point product having an initial boiling point above about 150
21 degrees C. The low pour point product of step (d) will generally consist of
22 diesel and lubricating base oil products, although depending on how the
23 operation is run the proportional yields of the products may vary over a
24 considerable range.

25
26 In one embodiment of the invention, the preferred dewaxing catalyst is a
27 hydroisomerization catalyst, such as, for example, a catalyst comprising a
28 silicoaluminophosphate molecular sieve, commonly referred to as a SAPO, in
29 combination with a hydrogenation component comprising an active metal.
30 The SAPO is preferably an intermediate pore SAPO, such as, for example,
31 SAPO-11, SAPO-31, and SAPO-41, with SAPO-11 being especially preferred.
32 Other aluminophosphates besides SAPO's can be used (broad category of
33 "non-zeolitic molecular sieves") and are taught in US Patent 5,135,638, col.
34 10, lines 24-31. A more complete description is in US Patent 5,883,837, col.

1 zeolite and at least one metal having hydrogenation activity, said dewaxing
2 being carried out under hydrodewaxing conditions selected to produce an C₅
3 plus intermediate having a lowered pour point relative to the C₅ plus syncrude
4 feedstock; (c) hydrofinishing the C₅ plus intermediate in a hydrofinishing zone
5 under hydrofinishing conditions, whereby a UV stabilized C₅ plus product is
6 produced; and (d) separately collecting from the UV stabilized C₅ plus product
7 an ultra high VI, low pour point lubricating base oil product. The term
8 "intermediate pore size" when referring to either a zeolite or a SAPO in this
9 disclosure means an inorganic molecular sieve having an effective pore
10 aperture in the range of from about 5.3 to about 6.5 Angstrom when the
11 porous inorganic oxide is in the calcined form. The most preferred zeolites for
12 producing ultra high VI products are somewhat more restricted having an
13 effective pore aperture of between about 5.0 to about 5.5 Angstrom.

14
15 In conventional processes for upgrading Fischer-Tropsch product into diesel
16 and lubricating base oils, the various fractions usually are separated prior to
17 upgrading. During dewaxing of that Fisher-Tropsch fraction boiling above
18 about 315 degrees C some wax cracking will occur which will yield lower
19 molecular products such as diesel, naphtha, and C₅ minus hydrocarbons.
20 When one of the preferred SAPO catalysts having high diesel selectivity, such
21 as SAPO-11, is used to dewax the fraction boiling in the lubricating base oil
22 range, diesel is preferentially produced as opposed to less valuable products
23 such as naphtha and C₅ minus hydrocarbons. In a conventional operation, a
24 second separation will generally be necessary following the dewaxing
25 operation, since considerable additional high value diesel is produced. In the
26 present invention only a single separation step is necessary to collect all of
27 the diesel which results in a significant cost saving. In addition, with the
28 present invention, the diesel fraction recovered from the dewaxing operation
29 will have an especially low pour point, preferably below about -20 degrees C
30 and more preferably below about -30 degrees C. The low pour point of the
31 diesel allows the end point to be extended which also increases the yield of
32 diesel in the overall product slate.

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2 The products may range from C_1 to C_{200} plus hydrocarbons with a majority in
3 the C_5 to C_{100} plus range. The reaction can be conducted in a variety of
4 reactor types, for example, fixed bed reactors containing one or more catalyst
5 beds, slurry reactors, fluidized bed reactors, or a combination of different type
6 reactors. Such reaction processes and reactors are well known and
7 documented in the literature. Slurry Fischer-Tropsch processes, which is a
8 preferred process in the practice of the present invention, utilize superior heat
9 (and mass) transfer characteristics for the strongly exothermic synthesis
10 reaction and are able to produce relatively high molecular weight, paraffinic
11 hydrocarbons when using a cobalt catalyst. In a slurry process, a syngas
12 comprising a mixture of hydrogen and carbon monoxide is bubbled up as a
13 third phase through a slurry in a reactor which comprises a particulate
14 Fischer-Tropsch type hydrocarbon synthesis catalyst dispersed and
15 suspended in a slurry liquid comprising hydrocarbon products of the synthesis
16 reaction which are liquid at the reaction conditions. The mole ratio of the
17 hydrogen to the carbon monoxide may broadly range from about 0.5 to about
18 4, but is more typically within the range of from about 0.7 to about 2.75 and
19 preferably from about 0.7 to about 2.5. A particularly preferred Fischer-
20 Tropsch process is taught in EP0609079, which is completely incorporated
21 herein by reference for all purposes.

22 Suitable Fischer-Tropsch catalysts comprise one or more Group VIII catalytic
23 metals such as Fe, Ni, Co, Ru and Re, with cobalt being preferred.
24 Additionally, a suitable catalyst may contain a promoter. Thus, a preferred
25 Fischer-Tropsch catalyst comprises effective amounts of cobalt and one or
26 more of Re, Ru, Pt, Fe, Ni, Th, Zr, Hf, U, Mg and La on a suitable inorganic
27 support material, preferably one which comprises one or more refractory
28 metal oxides. In general, the amount of cobalt present in the catalyst is
29 between about 1 and about 50 weight percent of the total catalyst
30 composition. The catalysts can also contain basic oxide promoters such as
31 ThO_2 , La_2O_3 , MgO , and TiO_2 , promoters such as ZrO_2 , noble metals (Pt, Pd,
32 Ru, Rh, Os, Ir), coinage metals (Cu, Ag, Au), and other transition metals such
33 as Fe, Mn, Ni, and Re. Suitable support materials include alumina, silica,

1 magnesia and titania or mixtures thereof. Preferred supports for cobalt
2 containing catalysts comprise titania. Useful catalysts and their preparation
3 are known and illustrated in U.S. Patent 4,568,663, which is intended to be
4 illustrative but non-limiting relative to catalyst selection.

5 6 CATALYTIC DEWAXING 7

8 Although not shown in the figure, it may be desirable to include a pretreatment
9 step for the syncrude prior to its introduction into the dewaxing unit, since raw
10 syncrude typically contains a number of contaminants which act as catalyst
11 poisons, most notably nitrogen and oxygen compounds. Both the nitrogen
12 and oxygen compounds may be removed by hydrotreating. Preferably the
13 nitrogen in the feed stock to the dewaxing reactor should be below 50 ppm
14 and more preferably below 10 ppm. Alternatively, the alcohols may be
15 dehydrated to remove water prior to dewaxing. Other methods for removing
16 contaminants include adsorption and extraction.

17
18 Catalytic dewaxing consists of three main classes, conventional
19 hydrodewaxing, complete hydroisomerization dewaxing, and partial
20 hydroisomerization dewaxing. All three classes involve passing a mixture of a
21 waxy hydrocarbon stream and hydrogen over a catalyst that contains an
22 acidic component to convert the normal and slightly branched iso-paraffins in
23 the feed to other non-waxy species, such as lubricating oil base stocks with
24 acceptable pour points. Typical conditions for all classes involve
25 temperatures from about 400 degrees F to about 800 degrees F (200 degrees
26 C to 425 degrees C), pressures from about 200 psig to 3000 psig, and space
27 velocities from about 0.2 to 5 hr⁻¹. The method selected for dewaxing a feed
28 typically depends on the product quality, and the wax content of the feed, with
29 conventional hydrodewaxing often preferred for low wax content feeds. The
30 method for dewaxing can be effected by the choice of the catalyst. The
31 general subject is reviewed by Avilino Sequeira, in *Lubricant Base Stock and*
32 *Wax Processing*, Marcel Dekker, Inc. pages 194-223. The determination
33 between conventional hydrodewaxing, complete hydroisomerization

1 dewaxing, and partial hydroisomerization dewaxing can be made by using the
 2 n-hexadecane isomerization test as described in U.S. Patent No. 5,282,958.
 3 When measured at 96 percent, n-hexadecane conversion using conventional
 4 hydrodewaxing catalysts will exhibit a selectivity to isomerized hexadecanes
 5 of less than 10 percent, partial hydroisomerization dewaxing catalysts will
 6 exhibit a selectivity to isomerized hexadecanes of greater than 10 percent to
 7 less than 40 percent, and complete hydroisomerization dewaxing catalysts will
 8 exhibit a selectivity to isomerized hexadecanes of greater than or equal to 40
 9 percent, preferably greater than 60 percent, and most preferably greater than
 10 80 percent.

11

12 In conventional hydrodewaxing, the pour point is lowered by selectively
 13 cracking the wax molecules mostly to smaller paraffins using a conventional
 14 hydrodewaxing catalyst, such as, for example ZSM-5. Metals may be added
 15 to the catalyst, primarily to reduce fouling. In the present invention
 16 conventional hydrodewaxing may be used to increase the yield of lower
 17 molecular weight products in the final product slate by cracking the Fischer-
 18 Tropsh wax molecules.

19

20 Complete hydroisomerization dewaxing typically achieves high conversion
 21 levels of wax by isomerization to non-waxy iso-paraffins while at the same
 22 time minimizing the conversion by cracking. Since wax conversion can be
 23 complete, or at least very high, this process typically does not need to be
 24 combined with additional dewaxing processes to produce a lubricating oil
 25 base stock with an acceptable pour point. Complete hydroisomerization
 26 dewaxing uses a dual-functional catalyst consisting of an acidic component
 27 and an active metal component having hydrogenation activity. Both
 28 components are required to conduct the isomerization reaction. The acidic
 29 component of the catalysts used in complete hydroisomerization preferably
 30 include an intermediate pore SAPO, such as SAPO-11, SAPO-31, and SAPO-
 31 41, with SAPO-11 being particularly preferred. Intermediate pore zeolites,
 32 such as ZSM-22, ZSM-23, SSZ-32, ZSM-35, and ZSM-48, also may be used
 33 in carrying out complete hydroisomerization dewaxing. Typical active metals
 34 include molybdenum, nickel, vanadium, cobalt, tungsten, zinc, platinum, and

1 palladium. The metals platinum and palladium are especially preferred as the
2 active metals, with platinum most commonly used.

3
4 In partial hydroisomerization dewaxing a portion of the wax is isomerized to
5 iso-paraffins using catalysts that can isomerize paraffins selectively, but only if
6 the conversion of wax is kept to relatively low values (typically below 50
7 percent). At higher conversions, wax conversion by cracking becomes
8 significant, and yield losses of lubricating base stock becomes uneconomical.
9 Like complete hydroisomerization dewaxing, the catalysts used in partial
10 hydroisomerization dewaxing include both an acidic component and a
11 hydrogenation component. The acidic catalyst components useful for partial
12 hydroisomerization dewaxing include amorphous silica aluminas, fluorided
13 alumina, and 12-ring zeolites (such as Beta, Y zeolite, L zeolite). The
14 hydrogenation component of the catalyst is the same as already discussed
15 with complete hydroisomerization dewaxing. Because the wax conversion is
16 incomplete, partial hydroisomerization dewaxing must be supplemented with
17 an additional dewaxing technique, typically solvent dewaxing, complete
18 hydroisomerization dewaxing, or conventional hydrodewaxing in order to
19 produce a lubricating base stock with an acceptable pour point (below about
20 +10 degrees F or -12 degrees C).

21
22 The present invention may also be used to prepare ultra-high VI lubricating
23 base oils. Catalysts containing SAPO's, such as SAPO-11, have been used
24 to produce ultra-high VI lubricating base oils. However, an intermediate pore
25 zeolite with one-dimensional pores, such as, for example, SSZ-32, ZSM-23,
26 and ZSM-22 also may be used in carrying out the present invention if a
27 lubricating base oil product having ultra high VI is desired. The term one-
28 dimensional pores, also referred to as 1-D pores, is fully explained in US
29 Patent 5,135,638, column 6, at lines 31-41. Briefly, the term refers to a zeolite
30 in which the intracrystalline channels are parallel and are not interconnected.
31 The production of ultra high VI lubricating base oil in this embodiment is
32 particularly surprising because with conventional petroleum-derived feeds,
33 catalysts containing SAPOs will usually produce a higher VI product than

those catalysts containing a zeolite. Preferably the intermediate pore zeolite is used in association with an active metal having hydrogenation activity.

In preparing those catalysts containing a non-zeolitic molecular sieve and having an hydrogenation component for use in the present invention, it is usually preferred that the metal be deposited on the catalyst using a non-aqueous method. Catalysts, particularly catalysts containing SAPO's, on which the metal has been deposited using a non-aqueous method have shown greater selectivity and activity than those catalysts which have used an aqueous method to deposit the active metal. The non-aqueous deposition of active metals on non-zeolitic molecular sieves is taught in US Patent 5,939,349. In general, the process involves dissolving a compound of the active metal in a non-aqueous, non-reactive solvent and depositing it on the molecular sieve by ion exchange or impregnation.

HYDROFINISHING

Hydrofinishing operations are intended to improve the UV stability and color of the products. It is believed this is accomplished by saturating the double bonds present in the hydrocarbon molecule, including those found in aromatics, especially polycyclic aromatics. In the process of the present invention, the C₅ plus intermediate recovered from the dewaxing operation is sent to a hydrofinisher. A general description of the hydrofinishing process may be found in US Patents 3,852,207 and 4,673,487. As used in this disclosure the term UV stability refers to the stability of the lubricating base oil or other products when exposed to ultraviolet light and oxygen. Instability is indicated when a visible precipitate forms or darker color develops upon exposure to ultraviolet light and air which results in a cloudiness or floc in the product. Lubricating base oils and diesel products prepared by the process of the present invention will require UV stabilization before they are suitable for use in the manufacture of commercial lubricating oils and marketable diesel.

Typically, the total pressure in the hydrofinishing zone will be between about 200 psig and about 3000 psig, with pressures in the range of about 500 psig

1 and about 2000 psig being preferred. Temperature ranges in the
2 hydrofinishing zone are usually in the range of from about 300 degrees F (150
3 degrees C) to about 700 degrees F (370 degrees C), with temperatures of
4 from about 400 degrees F (205 degrees C) to about 500 degrees F (260
5 degrees C) being preferred. The LHSV is usually within the range of from
6 about 0.2 to about 2.0, preferably 0.2 to 1.5 and most preferably from about
7 0.7 to 1.0. Hydrogen is usually supplied to the hydrofinishing zone at a rate of
8 from about 1000 to about 10,000 SCF per barrel of feed. Typically the
9 hydrogen is fed at a rate of about 3000 SCF per barrel of feed. The
10 hydrofinishing step may be integrated into the same gas system as the
11 dewaxing step.

12
13 Suitable hydrofinishing catalysts typically contain a Group VIII metal
14 component together with an oxide support. Metals or compounds of the
15 following metals are useful in hydrofinishing catalysts include nickel,
16 ruthenium, rhodium, iridium, palladium, platinum, and osmium. Preferably the
17 metal or metals will be platinum, palladium or mixtures of platinum and
18 palladium. The refractory oxide support usually consists of alumina, silica,
19 silica-alumina, silica-alumina-zirconia, and the like. The catalyst may
20 optionally contain a zeolite component. Typical hydrofinishing catalysts are
21 disclosed in US Patents 3,852,207; 4,157,294; and 4,673,487.

22
23 In carrying out the invention, the cut-point between those Fischer-Tropsch
24 fractions boiling in the range of diesel and lubricating base oil may be
25 adjusted to either increase the yield of diesel or the yield of lubricating base
26 oil. For example by extending the cut-point for diesel, it is possible to not only
27 maximize the yield of diesel but still also produce a diesel product having a
28 very low cloud point and pour point. At the same time, the volatility of the
29 lubricating base oil cut is minimized which is major commercial selling point
30 for lubricants.

31
32 When a SAPO, such as SAPO-11, is used as the hydroisomerization catalyst
33 in the dewaxing operation, diesel is the primary product of the wax-cracking.
34 Consequently, the actual yield for the less valuable naphtha and C₄ minus gas

1 is minimized. The cut-point between the diesel product and the lubricating
2 base oil product during fractionation may also be adjusted to decrease or
3 increase the amount of diesel present in the final product slate. For example,
4 the cut-point selected could be as low as 600 degrees F (515 degrees C).
5 This would increase the amount of lubricating base oil recovered at the
6 expense of diesel. Likewise, the cut-point could be selected as high as 700
7 degrees F (370 degrees C) or more. This would increase the amount of
8 diesel recovered at the expense of the yield of lubricating base oil. However,
9 in this later case the diesel recovered will have an especially low pour point
10 and the lubricating base oil will very low volatility.

11
12 Finally as already noted, the present process of the present invention requires
13 only a single fractionation operation instead of the two fractionation steps
14 which would be necessary using a conventional processing scheme.
15 Accordingly, the present invention results in a significant cost savings over
16 conventional operations.

17
18 The following example is intended to further illustrate a specific embodiment
19 of the invention without being interpreted as a limitation thereon.

20

21 EXAMPLE

22

23 A Fischer–Tropsch derived feedstock having the specifications shown in
24 Table 1 was dewaxed using a hydrocracking catalyst and a
25 hydroisomerization catalyst.

Table 1

API Gravity	49.0
Nitrogen, ppm	17
Sulfur, ppm	11
Oxygen, wt%	1.12
Simulated Distillation, TBP (°F)	
1/5 wt%	152/236
10/30	287/422
50	564
70/90	718/965
95/99	1062/1275

A commercially available nickel-Tungsten silica/alumina diesel hydrocracking catalyst was compared to a hydroisomerization catalyst containing 25 weight percent SAPO-11 on alumina with platinum present as the hydrogenation component. The feed was dewaxed at a total pressure of 1000 psig, a liquid hourly space velocity of 1.0, and a once through gas rate of 10,000 SCF H₂/bbl. The products recovered from the dewaxing operation were not hydrofinished and had the properties shown in Table 2.

Table 2

	Commercial Catalyst	Pt/SAPO-11
Catalyst Temp, F	672	736
Yields, wt%		
C4-	1.0	1.6
Naphtha (C5-300°F)	13.7	17.5
Diesel (300-700°F)	69.2	64.0
Base Oil (700°F+)	15.2	16.0
Diesel Properties		
Cloud Pt, °C	-9	-35
Vis@40°C, cSt	2.1	2.1
Base Oil Properties		
Pour Pt, °C	+13	-12
Vis@100°C, cSt	3.8	4.4
VI	133	158

Table 2 illustrates that the Fischer-Tropsch product may be bulk dewaxed and successfully produce satisfactory yields of diesel and lubricating base oil having excellent properties. The diesel recovered using the Pt/SAPO catalyst had a significantly lower cloud point than the diesel recovered using the conventional catalyst. When the lubricating base oils derived from the dewaxing operations are compared, it should be noted that the product derived using the Pt/SAPO catalyst had a significantly lower pour point and higher viscosity at 100 degrees C. In addition, the lubricating base oil product had a VI of 158 which is well in excess of that required to qualify as an ultra-high VI product.